

Description

USE OF CARBON COATING IN AN ELECTROCHEMICAL CELL

BACKGROUND OF INVENTION

[0001] This disclosure relates to a method and apparatus for using an elemental carbon coating in an electrochemical cell.

[0002] Electrochemical cells are energy conversion devices, usually classified as either electrolysis cells or fuel cells. A proton exchange membrane electrolysis cell can function as a hydrogen generator by electrolytically decomposing water to produce hydrogen and oxygen gas, and can function as a fuel cell by electrochemically reacting hydrogen with oxygen to generate electricity. Referring to Figure 1, which is a partial section of a typical anode feed electrolysis cell 100, process water 102 is fed into cell 100 on the side of an oxygen electrode (anode) 116 to form oxygen gas 104, electrons, and hydrogen ions (protons) 106. The reaction is facilitated by the positive terminal of a power source 120 electrically connected to

anode 116 and the negative terminal of power source 120 connected to a hydrogen electrode (cathode) 114. The oxygen gas 104 and a portion of the process water 108 exits cell 100, while protons 106 and water 110 migrate across a proton exchange membrane 118 to cathode 114 where hydrogen gas 112 is formed.

[0003] Another typical water electrolysis cell using the same configuration as is shown in Figure 1 is a cathode feed cell, wherein process water is fed on the side of the hydrogen electrode. A portion of the water migrates from the cathode across the membrane to the anode where hydrogen ions and oxygen gas are formed due to the reaction facilitated by connection with a power source across the anode and cathode. A portion of the process water exits the cell at the cathode side without passing through the membrane.

[0004] A typical fuel cell uses the same general configuration as is shown in Figure 1. Hydrogen gas is introduced to the hydrogen electrode (the anode in fuel cells), while oxygen, or an oxygen-containing gas such as air, is introduced to the oxygen electrode (the cathode in fuel cells). Water can also be introduced with the feed gas. The hydrogen gas for fuel cell operation can originate from a pure hydrogen

source, hydrocarbon, methanol, or any other hydrogen source that supplies hydrogen at a purity suitable for fuel cell operation (i.e., a purity that does not poison the catalyst or interfere with cell operation). Hydrogen gas electrochemically reacts at the anode to produce protons and electrons, wherein the electrons flow from the anode through an electrically connected external load, and the protons migrate through the membrane to the cathode. At the cathode, the protons and electrons react with oxygen to form water, which additionally includes any feed water that is dragged through the membrane to the cathode. The electrical potential across the anode and the cathode can be exploited to power an external load.

[0005] In other embodiments, one or more electrochemical cells can be used within a system to both electrolyze water to produce hydrogen and oxygen, and to produce electricity by converting hydrogen and oxygen back into water as needed. Such systems are commonly referred to as regenerative fuel cell systems.

[0006] Electrochemical cell systems typically include a number of individual cells arranged in a stack, with the working fluids directed through the cells via input and output conduits formed within the stack structure. The cells within

the stack are sequentially arranged, each including a cathode, a proton exchange membrane, and an anode. Each cathode/membrane/anode assembly (hereinafter "membrane electrode assembly", or "MEA") typically comprises a first flow field in fluid communication with the cathode and a second flow field in fluid communication with the anode. The MEA may furthermore be supported on both sides by screen packs or bipolar plates disposed within flow fields. Screen packs or bipolar plates may facilitate fluid movement to and from the MEA, membrane hydration, and may also provide mechanical support for the MEA.

[0007] In order to maintain intimate contact between cell components under a variety of operational conditions and over long time periods, uniform compression is applied to the cell components. Pressure pads or other compression means are often employed to provide even compressive force from within the electrochemical cell. Pressure pads may be fabricated from materials incompatible with system fluids and/or the cell membrane, thereby requiring the pressure pad to be disposed within a protective encasing or otherwise isolated from the system fluids.

[0008] However, while existing internal components are suitable

for their intended purposes, there still remains a need for improvement, particularly regarding enhancing electrical conductivity within the cell and providing inert surfaces. Therefore, a need exists for a protective coating on internal components of an electrochemical cell, preferably a coating that is electrically conductive.

SUMMARY OF INVENTION

[0009] Some of the above-described drawbacks and disadvantages are alleviated by some embodiments of the invention.

[0010] In an embodiment, an electrochemical cell includes a first electrode, a second electrode, and a membrane disposed between and in fluid communication with the first and second electrodes. A first cell separator plate opposes the first electrode and defines a first flow field therebetween, the first flow field being proximate a first frame member. A second cell separator plate opposes the second electrode and defines a second flow field therebetween, the second flow field being proximate a second frame member. The first cell separator plate, the second cell separator plate, the first frame member, the second frame member, or a combination thereof, are at least partially coated with a layer containing elemental carbon.

[0011] In another embodiment, a method of coating a surface of an electrochemical cell includes: preparing a coating composition having a liquid dispersion of elemental carbon, the liquid dispersion having elemental carbon particles, a dispersing medium and a dispersing agent; and applying the liquid dispersion to the surface of the electrochemical cell to provide an elemental carbon layer thereon.

[0012] In a further embodiment, a method of coating a surface of an electrochemical cell is disclosed. A coating composition is prepared having a liquid dispersion of elemental carbon, the liquid dispersion including elemental carbon particles, a dispersing medium and a dispersing agent. The surface of the electrochemical cell is rinsed, cleaned, and conditioned to remove surface contaminants therefrom and to promote adhesion of the elemental carbon particles. The liquid dispersion is then applied to the surface, which is then fixed to remove excess carbon deposits and dried to provide an elemental carbon layer thereon.

[0013] In yet another embodiment, a surface of an electrochemical cell is disclosed having been prepared by a method that produces a surface electrical resistivity of equal to or less than about 1000 ohm-cm.

[0014] In yet a further embodiment, a surface of an electrochemical cell is prepared by a method including electroplating the surface of the electrochemical cell to provide an elemental carbon layer thereon, the elemental carbon layer having an electrical resistivity of equal to or less than about 1000 ohm-cm.

[0015] The above described and other features are exemplified by the following figures and detailed description.

BRIEF DESCRIPTION OF DRAWINGS

[0016] Referring now to the figures wherein the like elements are numbered alike: Figure 1 is a schematic diagram of a partial electrochemical cell showing an electrochemical reaction for use in accordance with embodiments of the invention; and Figure 2 is an expanded schematic diagram of an exemplary electrochemical cell for implementing an embodiment of the invention.

DETAILED DESCRIPTION

[0017] Disclosed herein are novel methods and apparatus for an electrochemical cell having an elemental carbon coating over various components of the cell.

[0018] Although the disclosure below is described in relation to a proton exchange membrane electrochemical cell employ-

ing hydrogen, oxygen, and water, other types of electrochemical cells and/or electrolytes may be used, including, but not limited to, phosphoric acid, solid oxide, and potassium hydroxide, and the like. Various reactants can also be used, including, but not limited to, hydrogen bromine, oxygen, air, chlorine, and iodine. Upon the application of different reactants and/or different electrolytes, the flows and reactions are understood to change accordingly, as is commonly understood in relation to that particular type of electrochemical cell.

[0019] Referring to Figure 2, an electrochemical cell (cell) 200 suitable for operation as an anode feed electrolysis cell, cathode feed electrolysis cell, fuel cell, or regenerative fuel cell is schematically shown. Thus, while the discussion below is directed to an anode feed electrolysis cell, cathode feed electrolysis cells, fuel cells, and regenerative fuel cells are also contemplated. Cell 200 is typically one of a plurality of cells employed in a cell stack as part of an electrochemical cell system. When cell 200 is used as an electrolysis cell, power inputs are generally between about 1.48 volts and about 3.0 volts, with current densities between about 50 A/ft² (amperes per square foot) and about 4,000 A/ft². When used as a fuel cells power out-

puts range between about 0.4 volts and about 1 volt, and between about 0.1 A/ft² and about 10,000 A/ft². The number of cells within the stack, and the dimensions of the individual cells is scalable to the cell power output and/or gas output requirements.

[0020] Cells are typically operated at pressures up to or exceeding about 100 psi, preferably about 500 psi, most preferably about 2500 psi, or even more preferably about 10,000 psi. Cell 200 includes a membrane 202 having a first electrode (e.g., an anode) 204 and a second electrode (e.g., a cathode) 206 disposed on opposite sides thereof. Flow fields 210, 220, which are in fluid communication with electrodes 204 and 206, respectively, are defined generally by the regions proximate to, and bounded on at least one side by, each electrode 204 and 206 respectively. A flow field member 228 may be disposed within flow field 220 between electrode 206 and, optionally, a pressure pad separator plate 222. A pressure pad 230 is typically disposed between pressure pad separator plate 222 and a cell separator plate 232. Cell separator plate 232 is disposed adjacent to pressure pad 230. A frame 224 generally surrounds flow field 220 and an optional gasket 226 is disposed between frame 224 and pressure

pad separator plate 222 generally for enhancing the seal within the reaction chamber defined on one side of cell 200 by frame 224, pressure pad separator plate 222 and electrode 206. Gasket 236 may be disposed between pressure pad separator plate 222 and cell separator plate 232 enclosing pressure pad 230.

[0021] Another flow field member 218 may be disposed in flow field 210. A frame 214 generally surrounds flow field member 218, a cell separator plate 212 is disposed adjacent flow field member 218 opposite oxygen electrode 204, and a gasket 216 is disposed between frame 214 and cell separator plate 212, generally for enhancing the seal within the reaction chamber defined by frame 214, cell separator plate 212, and the oxygen side of membrane 202. The cell components, particularly cell separator plates 212, 232, frames 214, 224, and gaskets 216, 226, and 236 are formed with the suitable manifolds or other conduits as is conventional.

[0022] Membrane 202 comprises electrolytes that are preferably solids or gels under the operating conditions of the electrochemical cell. Useful materials include proton conducting ionomers and ion exchange resins. Useful proton conducting ionomers include complexes comprising an alkali

metal salt, alkali earth metal salt, a protonic acid, or a protonic acid salt. Useful complex-forming reagents include alkali metal salts, alkaline metal earth salts, and protonic acids and protonic acid salts. Counter-ions useful in the above salts include halogen ion, perchloric ion, thiocyanate ion, trifluoromethane sulfonic ion, borofluoric ion, and the like. Representative examples of such salts include, but are not limited to, lithium fluoride, sodium iodide, lithium iodide, lithium perchlorate, sodium thiocyanate, lithium trifluoromethane sulfonate, lithium borofluoride, lithium hexafluorophosphate, phosphoric acid, sulfuric acid, trifluoromethane sulfonic acid, and the like. The alkali metal salt, alkali earth metal salt, protonic acid, or protonic acid salt is complexed with one or more polar polymers such as a polyether, polyester, or polyimide, or with a network or cross-linked polymer containing the above polar polymer as a segment. Useful polyethers include polyoxyalkylenes, such as polyethylene glycol, polyethylene glycol monoether, and polyethylene glycol diether; copolymers of at least one of these polyethers, such as poly(oxyethylene-co-oxypropylene) glycol, poly(oxyethylene-co-oxypropylene) glycol monoether, and poly(oxyethylene-co-oxypropylene) glycol diether;

condensation products of ethylenediamine with the above polyoxyalkylenes; and esters, such as phosphoric acid esters, aliphatic carboxylic acid esters or aromatic carboxylic acid esters of the above polyoxyalkylenes. Copolymers of, e.g., polyethylene glycol with dialkylsiloxanes, maleic anhydride, or polyethylene glycol monoethyl ether with methacrylic acid are known in the art to exhibit sufficient ionic conductivity to be useful.

[0023] Ion-exchange resins useful as proton conducting materials include hydrocarbon- and fluorocarbon-type resins. Hydrocarbon-type ion-exchange resins include phenolic resins, condensation resins such as phenol-formaldehyde, polystyrene, styrene-divinyl benzene copolymers, styrene-butadiene copolymers, styrene-divinylbenzene-vinylchloride terpolymers, and the like, that are imbued with cation-exchange ability by sulfonation, or are imbued with anion-exchange ability by chloromethylation followed by conversion to the corresponding quaternary amine.

[0024] Fluorocarbon-type ion-exchange resins can include hydrates of tetrafluoroethylene-perfluorosulfonyl ethoxyvinyl ether or tetrafluoroethylene-hydroxylated (perfluoro vinyl ether) copolymers. When oxidation and/or

acid resistance is desirable, for instance, at the cathode of a fuel cell, fluorocarbon-type resins having sulfonic, carboxylic and/or phosphoric acid functionality are preferred. Fluorocarbon-type resins typically exhibit excellent resistance to oxidation by halogen, strong acids and bases. One family of fluorocarbon-type resins having sulfonic acid group functionality is NAFION™ resins (commercially available from E. I. du Pont de Nemours and Company, Wilmington, DE).

[0025] Electrodes 204 and 206 comprise catalyst suitable for performing the needed electrochemical reaction (i.e., electrolyzing water and producing hydrogen). Suitable catalyst include, but are not limited to, materials comprising platinum, palladium, rhodium, carbon, gold, tantalum, tungsten, ruthenium, iridium, osmium, alloys of at least one of the foregoing catalysts, and the like. Electrodes 204 and 206 can be formed on membrane 202, or may be layered adjacent to, but in contact with, membrane 202. Both techniques are known in the art.

[0026] Flow field members 218, 228 may be screen packs, bipolar plates, or other support members. Any screen or bipolar plate capable of supporting membrane 202, allowing the passage of system fluids, and preferably conducting

electrical current is suitable. The screens can comprise layers of perforated sheets or a woven mesh formed from metal or strands. These screens are typically comprised of metals, such as, for example, niobium, zirconium, tantalum, titanium, carbon steel, stainless steel, nickel, cobalt, and alloys comprising at least one of the foregoing metals. The geometry of the openings in the screens can range from ovals, circles, and hexagons to diamonds and other elongated shapes. Bipolar plates are commonly porous structures comprising fibrous carbon or fibrous carbon impregnated with polytetrafluoroethylene or PTFE (commercially available under the trade name TEFLON® from E. I. du Pont de Nemours and Company).

[0027] Pressure pad 230 provides for uniform compression between cell components, and may comprise a resilient member, preferably an elastomeric material. Suitable elastomeric materials include, but are not limited to silicones, such as, for example, fluorosilicones; fluoroelastomers, such as KALREZ® (commercially available from E. I. du Pont de Nemours and Company), VITON® (commercially available from E. I. du Pont de Nemours and Company), and FLUOREL® (commercially available from Minnesota Mining and Manufacturing Company, St. Paul, MN); and combina-

tions thereof.

[0028] Pressure pad 230 also comprises an electrically conductive material. The electrically conductive material is preferably compatible with the system fluids and membrane 202. Suitable electrically conductive materials include, but are not limited to, conductive metals and alloys and superalloys thereof, for example niobium; zirconium; tantalum; titanium; niobium; iron and iron alloys, for examples steels such as stainless steel; nickel and nickel alloys such as HASTELLOY®(commercially available from Haynes International, Kokomo, IN); cobalt and cobalt superalloys such as ELGILOY®(commercially available from Elgiloy® Limited Partnership, Elgin, IL) and MP35N® (commercially available from Maryland Specialty Wire, Inc., Rye, NY); hafnium, tungsten, and alloys, superalloys, and mixtures comprising at least one of the foregoing, with titanium preferred. Conductive carbon may also be used. When used without pressure pad separator plate 222, pressure pad 230 can be porous to allow passage of water or system gases.

[0029] Cell components are typically plated with protective and/or conductive layers. This plating is often electrolytic and involves significant time, labor, and expense both in the

plating process and the environmental restrictions surrounding electroplating processes.

[0030] It has been discovered that various components of an electrolytic cell, such as electrochemical cell 200 in Figure 2, when coated with an elemental carbon-containing composition to produce a layer 300 of elemental carbon thereon, are provided with superior protection against corrosion, improved electrical conductivity, and realize a significant cost reduction in producing electrochemical cells. While Figure 2 depicts layer 300 only on a surface of cell separator plate 212, it will be appreciated that all or portions of surfaces of other components of electrochemical cell 200 may also be coated, such as on frame 214, flow field member 218, pressure pad separator plate 222, frame 224, flow field member 228, pressure pad 230, and cell separator plate 232, for example.

[0031] The coating composition comprises elemental carbon, a carrier or dispersing medium, and at least one dispersing agent. Optionally, the coating composition may contain at least one binding agent, surfactant, pH buffer, chelating agent, or conditioning agent.

[0032] The elemental carbon may be in many forms and geometries, such as fibrous for example. Various types of con-

ductive carbon fibers may be classified according to their diameter, morphology, and degree of graphitization (morphology and degree of graphitization being interrelated). These characteristics are presently determined by the method used to synthesize the carbon fiber. For example, carbon fibers having diameters down to about 5 micrometers, and graphene ribbons parallel to the fiber axis (in radial, planar, or circumferential arrangements) are produced commercially by pyrolysis of organic precursors in fibrous form, including phenolics, polyacrylonitrile (PAN), or pitch. These types of fibers have a relatively lower degree of graphitization.

[0033] Small carbon fibers having diameters of about 3 to about 2000 nanometers (nm), and "tree-ring" or "fishbone" structures are presently grown from hydrocarbons in the vapor phase, in the presence of particulate metal catalysts at moderate temperatures, i.e., about 800 to about 1500°C. Small carbon fibers are generally cylindrical, and have a hollow core. In the "tree-ring" structure, a multiplicity of substantially graphitic sheets is coaxially arranged about the core, wherein the c-axis of each sheets is substantially perpendicular to the axis of the core. The interlayer correlation is generally low. In the "fishbone"

structure, the fibers are characterized by graphite layers extending from the axis of the hollow core, as shown in EP 198 558 to Geus. A quantity of pyrolytically-deposited carbon may also be present on the exterior of the fiber.

[0034] Carbon nanotubes, in contrast, are presently produced by laser-evaporation of graphite or carbon arc synthesis, yielding fullerene related structures, which generally have of graphene cylinders, which may be open, or closed at either end with caps containing pentagonal and/or hexagonal rings. Nanotubes may have a single wall or have multiple concentrically arranged walls, and have diameters of about 0.7 nm to about 2.4 nm for the single-wall nanotubes and about 2 nm to about 50 nm for the multi-wall nanotubes having multiple concentrically arranged walls. In the multi-layer structure the cross-section of the hollow core becomes increasingly small with increasing numbers of layers. At diameters larger than about 10 to about 20 nm, multi-wall nanotubes begin to exhibit a hexagonal pillar shape, such that the curvature of the nanotubes becomes concentrated at the corners of the pillars. This arises from the interlayer correlation becoming established over a larger area with a structure close to that of graphite. This faceting is not found in the vapor-grown,

using a thermal chemical vapor deposition process for example, small carbon fibers described above, although it is possible to produce nanotubes from the vapor phase using much lower hydrocarbon pressures, and although the innermost tubes of some vapor grown carbon fibers are considered to be carbon nanotubes.

[0035] Carbon nanotubes produced by laser-evaporation of graphite or carbon arc synthesis may also be used. When nanotubes are used it is preferred to have an average aspect ratio greater than or equal to about 5, preferably greater than or equal to about 100, and more preferably greater than or equal to about 1,000. Representative carbon nanotubes are described in U. S. Patent No. 6,183,714 to Smalley et al., U.S. Patent No. 5,591,312 to Smalley, U.S. Patent No. 5,641,455 to Ebbesen et al., U.S. Patent No. 5,830,326 to Iijima et al., U.S. Patent No. 5,591,832 to Tanaka et al., and U.S. Patent No. 5,919,429 to Tanaka et al.

[0036] If employed, the small carbon fibers may be present in an amount of about 1 weight percent (wt%) to about 50 wt%. Within this range, the small carbon fibers may be employed in an amount of less than or equal to about 30 wt%, with less than or equal to about 25 wt% more pre-

ferred. Also preferred within this range is an amount of small carbon fibers of greater than or equal to about 10 wt%, with greater than or equal to about 20 wt% more preferred. All weight percent disclosed herein are based upon the total dry weight of the coating composition unless otherwise specified.

[0037] Other types of elemental carbon include, for example, fullerene (C₆₀), carbon black, graphite, or a combination thereof comprising at least one of the foregoing. As used herein, carbon black is characterized as being amorphous in contrast to graphite, which is highly crystalline. Typically, carbon black is impure, frequently being associated with volatile contaminants. In contrast, graphite, and in particular synthetic graphite, is relatively pure.

[0038] Several commercial grades of suitable carbon black include, for example, CABOT MONARCH 1300 and CABOT XC-72R Conductive (Cabot Corporation, Boston, Mass.); ACHESON ELECTRODAG 230 (Acheson Colloids Co., Port Huron, Mich.); COLUMBIAN RAVEN 3500 (Columbian Carbon Co., New York City, N.Y.); and the like having similar particle sizes and dispersion characteristics.

[0039] Graphite may be either synthetic or naturally occurring. Accordingly, suitable commercial graphite and graphite

dispersions contemplated to be useful herein include: UL-TRAFINE GRAPHITE (Showa Denko K.K., Tokyo, Japan); AQUADAGE E; MICRO 440 and GRAPHITE 850 (Asbury Graphite Mills Inc., Asbury, N.J.); GRAFO 1204B (Metal Lubricants Company, Harvey, Ill.); GRAPHOKOTE 90 (Dixon Products, Lakehurst, N.J.); NIPPON AUP (0.7 micron) (Nippon Graphite Industries, Ltd., Ishiyama, Japan) and the like having similar electrical and dispersion characteristics, with synthetic graphite being preferred.

[0040] Synthetic graphite can be formed by various methods, including, for example, heat-treating (graphitizing) a carbon source at temperatures exceeding about 2,400°C. The most preferred conductive graphite, commonly referred to as electronic grade, is prepared at very high graphitization temperatures (e.g., about 3,000°C or so). The elemental carbon is present in the coating composition in an amount effective to provide an electrically conductive coating when the composition is applied to a substrate. The elemental carbon may be present in the coating composition in an amount of about 5 wt% to about 25 wt%. Within this range, the elemental carbon may be present in an amount of greater than or equal to about 10 wt%. Also preferred within this range, the elemental carbon may be present in

an amount of less than or equal to about 20 wt%.

[0041] The elemental carbon when provided in particulate form, generally has a mean particle size of about 15 nm to about 50 nm. Within this range, the mean particle size is preferably greater than or equal to about 20 nm, with greater than or equal to about 30 nm preferred. Also preferred within this range is a mean particle size of less than or equal to about 40 nm, with less than or equal to about 35 nm, more preferred.

[0042] Graphite particles of suitable size can also be prepared by various methods including, for example, wet grinding or milling of raw graphite to form a slurry, graphitizing carbon-containing particles, and the like.

[0043] A combination of carbon black and graphite can be used, wherein the carbon black preferably has a substantially smaller particle size (i.e., sub-micron average diameter) than the graphite particles. The weight to weight ratio of graphite to carbon black is at least about 1:100, or at least about 100:1, or at most about 1:100, or at most about 100:1.

[0044] While not bound by any theory as to why the admixture of carbon black and graphite may be desirable, the inventors submit that graphite and carbon black may be synergistic

in the contemplated coating compositions because graphite is more conductive but hard to grind to sub-micron size, while carbon black is normally sub-micron-sized but less conductive. The smaller carbon black particles may form low-resistance paths in the interstices between the larger graphite particles, thus reducing the interstitial electrical resistance of the coating. The size of the materials combined thus determines the optimum ratio of the two. In comparing the functional characteristics of a surface coated with elemental carbon as opposed to one coated with non-elemental carbon, it has been found that surface electrical conductivity and surface inertness improve with the use of elemental carbon.

[0045] The carrier or dispersing medium of the composition may be organic (i.e., substantially water free) or may be an aqueous dispersing medium, which, as used herein, includes any solvent that is equal to or greater than about 1 wt% water, wherein the balance of the material is a water-soluble composition. Typical water-soluble compositions include the low molecular weight alcohols, such as methanol, ethanol, and isopropanol. Additional solvents such as dimethylsulfoxide, tetrahydrofuran, and ethylene or propylene glycol may also be used. Alternatively, the

aqueous dispersing medium may be water with deionized water being preferred.

[0046] Suitable binding agents are either non-water soluble, or water-soluble, and possess properties consistent with binding to the carbon particles. The binding agent is believed to assist the dispersed carbon particles in adhering to the surface of the substrate. The binding agent, should be present, if at all, in an amount effective to bind the carbon particles to a substrate. The binding agent can be presented in an amount of about 5 wt% to about 50 wt%. Within this range the binder can be present in an amount of greater than or equal to about 10 wt%, with greater than or equal to about 15 wt% preferred. Also within this range, the binding agent can be present in an amount of less than or equal to about 30 wt%, with less than or equal to about 25 wt% preferred.

[0047] A suitable binding agent is any natural or synthetic polymer, polymerizable monomer, or the like, as well as combinations comprising at least one of these binders, capable of both adhering to the carbon particles and, optionally, receiving an anionic dispersing agent (as described below). Alternatively, the binding agent can be capable of dispersing the carbon particles to which it adheres in the

aqueous medium of the dispersion. For example, the binding agent may be a water-soluble or water dispersible material selected from the group consisting of monosaccharides, polysaccharides, and ionic polymers. In an embodiment, a 10 wt% aqueous test solution of the binding agent has a viscosity of equal to or greater than about 10 cps (centipoise) at about 25°C, and equal to or less than about 15 cps at about 25°C.

[0048] Suitable monosaccharide binding agents include tetroses, pentoses, and hexoses. Suitable polysaccharide (which for the present purposes includes disaccharide and higher saccharide) binding agents include sucrose, maltose, fructose, lactose, stachyose, maltopentose, dextrin, cellulose, corn and other starches, and polysaccharide gums. Suitable polysaccharide gums include agar, arabic, xanthan, for example, KELZAN industrial grade xanthan gum, (Kelco Div. of Merck & Co, Inc. of Rahway, N.J.), pectin, alginate, tragacanth, dextran, and the like. Suitable derivative polysaccharides include cellulose acetates, cellulose nitrates, methylcellulose, and carboxymethylcellulose. Suitable hemi-cellulose polysaccharides include d-gluco-d-mannans, d-galacto-d-gluco-d-mannans, and the like. Suitable ionic polymers include anionic polymers

such as, for example, alkylcellulose, carboxyalkylcelluloses and salts thereof, cellulose ethers, nitrocellulose, and the like. Specific examples of suitable anionic polymers include KLUCEL hydroxypropylcellulose; AQUALON CMC 7L sodium carboxymethylcellulose, and NATROSOL hydroxyethylcellulose (Aqualon Company of Hopewell, Va.); ethylcellulose, (Hercules of Wilmington, Del.); METHOCEL cellulose ethers (Dow Chemical Co., Midland, Mich.); and the like.

[0049] Suitable acrylics for use as binding agents include polymerizable monomers and polymers, such as, for example, emulsion polymers commonly known as acrylic latices. Suitable monomers include acrylamide, acrylonitrile, acrylic acid, methacrylic acid, glycidyl methacrylate, and the like. Suitable acrylic polymers include polymers of any one or more of the foregoing monomers; polyacrylamide polymers such as, for example, SEPARAN NP10, SEPARAN-MGL, SEPARAN 870, and SEPARAN MG200 polymers (Springfield Scientific Supplies, Springfield, OR); polyacrylic acid; acrylic ester polymers such as polymethyl acrylate, polyethyl acrylate, polypropyl acrylate, polyisopropyl acrylate, polybutyl acrylate, polyisobutyl acrylate, polypentyl acrylate, polyhexyl acrylate, polyheptyl acry-

late, polyoctyl acrylate, and polyisobornyl acrylate; and like polyacrylates. Suitable acrylics available to the trade include NALCO 603, PURIFLOC C31, and ACRYCOL acrylics (Rohm and Haas Company, Philadelphia, Pa.).

[0050] Other suitable binding agents include vinyl resins such as, for example, polyvinyl acetates, polyvinyl ethers, and polyvinyl chlorides. Suitable pyrrolidinone resins include poly(N-vinyl-2-pyrrolidinone) and the like. Representative trade materials include PVP K-60 resin, PVP/VA E335 resin, PVP/VA 1535 resin, and the like (GAF Corporation.) Suitable polyols include polyvinyl alcohols including ELVANOL 90-50, ELVANOL HV, ELVANOL 85-80, and the like (du Pont de Nemours and Company, Wilmington, DE.) Cationic resins and other materials suitable for use as binding agents include, for example, polyethylenimine, methylaminoethyl resins, alkyltrimethylammonium chlorides, and the like; esters of olefinic alcohols, aminoalkyl esters, esters of ether alcohols, cycloalkyl esters, and esters of halogenated alcohols are also suitable for use as binding agents. Suitable polyethylene oxides include materials available under the trade names NSR N-10, NSR N3000, and NSR 301 (Union Carbide Corp.) Still more suitable binding agents include epoxy resins, cresol no-

volac resins, phenol novolac resins; epichlorohydrin resins; bisphenol resins; phenolic resins, such as, for example, DURITE AL-5801A (Borden Packaging and Industrial Products, Louisville, Ky.); natural resins and polymerizable materials such as damar, manila, rosin gum, rosin wood, rosin tall oil, and the like.

[0051] A practical upper limit to the amount of binding agent is an amount, which materially interferes with the conductivity of the resulting conductive coatings by diluting the conductive solids in the composition after it is deposited as a film, layer, or coating.

[0052] Suitable dispersing agents include anionic dispersing agents having a weight average molecular weight equal to or less than about 1000 Daltons, present in an amount sufficient to cause the bound carbon particles to disperse in the dispersing medium. The amount of dispersing agent used being dependent upon the size of the carbon particles, and the amount of binding agent bound thereto. As a general rule, smaller carbon particles require less dispersing agent than would be required to disperse larger particles. A practical upper limit to the amount of anionic dispersing agents used is an amount that materially interferes with the conductivity of the resulting con-

ductive coatings by diluting the conductive solids in the composition after it is deposited on the substrate. Anionic dispersing agent may be present in an amount of about 5 wt% to about 50 wt%. Within this range the dispersing agent may be present in an amount of greater than or equal to about 10 wt%, with greater than or equal to about 15 wt% preferred. Also within this range, the dispersing agent may be present in an amount of less than or equal to about 30 wt%, with less than or equal to about 25 wt% preferred.

[0053] Suitable anionic dispersing agents include, for example, acrylic latices, aqueous solutions of alkali metal polyacrylates, and the like. Some of the previously defined binding agents, which have an anionic character are also contemplated to be suitable as an anionic dispersing agent herein. Specific examples of suitable anionic dispersing agents include ACRY SOL I-1955 and ACRY SOL I-545 (Rohm and Haas Co., Philadelphia, Pa.) The composition and method is capable of being run over a wide pH range. Most broadly, the composition may have a pH that does not entirely destroy its utility, typically a pH of about 3 to about 8. Within this range, the pH is preferably greater than or equal to about 5, with greater than or equal to

about 6 more preferred. Also within this range, a pH of less than or equal to about 7.5 is preferred, with less than or equal to about 7 more preferred.

[0054] The pH of the dispersion may be maintained by employing a pH buffer. The buffer functions by precluding or minimizing changes in pH such as may occur during the course of a run as a large number of surfaces are treated. The maintenance of a constant or nearly constant pH ensures that the conductive coating is applied reproducibly from surface to surface. Another advantage of using a buffer system is that the normalities of one or more buffer components can be measured and adjusted to maintain proper process control. Suitable buffers include carbonate-bicarbonate, phosphate, acetate, borate, barbitol, and the like, which are well known in the art. The anions of the buffer may be associated with any suitable cation, such as an alkali metal cation, metal cation, ammonium cation or the like.

[0055] In addition to the buffer, a surfactant may be employed. A suitable surfactant will decrease the surface tension of the dispersing medium to allow the dispersed carbon particles to uniformly coat the substrate. A second function of the surfactant is to wet the surfaces of the substrate. Both fa-

cilitate the coating of these surfaces with the carbon dispersion.

[0056] The amount of surfactant will vary depending upon the surfactant itself, although additional amounts of surfactant could be added, once the critical micelle concentration is achieved, they addition might not provide any additional benefit. When coating non-flat or porous surfaces such as different embodiments of the flow field members, an increasing amount of surfactant is recommended especially with decreasing through-hole size in the member. When needed, the composition should contain sufficient surfactant to allow the aqueous dispersing medium to freely carry the dispersed carbon particles throughout the flow field members having through holes of various sizes. The composition typically contains surfactant in an amount of about 5 wt% to about 50 wt%. Within this range the surfactant can be present in an amount of greater than or equal to about 10 wt%, with greater than or equal to about 15 wt% preferred. Also within this range, the surfactant can be present in an amount of less than or equal to about 30 wt%, with less than or equal to about 25 wt% preferred.

[0057] Suitable surfactants include, for example, TRITON X-100

(Rohm and Haas Co., Philadelphia, Pa.); MAPHOS 56 (Mazer Chemicals, Inc.); TAMOL 819L-43, 850, and 960 (Rohm and Haas Co., Philadelphia, Pa.); FLUORAD.RTM. FC-120, FC-430, FC-431, FC-129, and FC-135 (Minnesota Mining & Manufacturing Co., St. Paul, Minn.); DARVAN No. 1, (R. T. Vanderbilt Co.); ECCOWET LF (Eastern Color and Chemical); PETROULF (Petro Chemical Co. Inc.); POLYTERGENT B-SERIES (Olin Corporation); and the like. Cationic and other surfactants may also be used, depending upon the pH and other characteristics of the composition.

[0058] The resulting composition is a carbon dispersion that is capable of depositing a uniform, low resistivity coating of carbon particles on the surfaces of the cell components. The composition may be used "as is," or it may be sold in concentrate form and then diluted up to tenfold (10:1) or so, preferably up to fourfold (4:1), at the point of use. The composition may be diluted with any dispersing medium, which may include one or more buffers, dispersing agents, surfactants, or other components including those listed above.

[0059] The coating composition can be used to provide a conductive carbon layer on the surface of a substrate. In par-

ticular, this process comprises preparing any of the liquid dispersions of carbon, as described previously, which are capable of depositing a coating of carbon on the surfaces; applying the liquid dispersion to the surfaces of the cell to form a dispersion coating thereon; and optionally, separating substantially all of the aqueous dispersing medium from the carbon particles, typically by drying the dispersion, so the carbon particles are deposited on the surface in a substantially continuous layer.

[0060] A preferred method of applying the carbon layer includes rinsing, cleaning, conditioning, adhesion promotion, fixing, and microetching as described below. The method can be carried out in a variety of equipment, for example, vertical or dip process equipment, in which the reagents are in stationary baths into which the vertically-disposed substrates are sequentially dipped, and conveyorized or horizontal equipment in which the substrates are flooded or sprayed with the respective reagents while disposed and traveling substantially horizontally. Either type of equipment, or any combination of the two types of equipment, may be used.

[0061] Commonly, the process includes first rinsing, and then cleaning the substrate to be covered. In rinsing, the sub-

strate is thoroughly wetted and contaminants such as grease, oil, and dirt are removed from the substrate. The substrate may then be cleaned by contacting it with an alkaline aqueous solution or dispersion of a surfactant, which preferably is either cationic or nonionic. A chelating agent may also be added to the composition to provide a uniform solution. Optionally, particularly if the base employed is an alkali metal salt, a buffer may be added to the composition.

[0062] The chelating agents contemplated herein include alkali metal salts of ethylenediaminetetraacetic acid (EDTA), for example, sodium EDTA. Other suitable chelating agents are readily known to those of ordinary skill in the art.

[0063] A surface to be processed is commonly dip-processed in the cleaning solution for up to about 15 minutes or so at about 100 °C to about 150 °C, or cleaned in a conveyORIZED process by flooding it at a similar temperature for a similar time.

[0064] Rinsing steps are optionally added between various reagent baths to prolong the life of the subsequent reagent baths. Typically, the rinsing medium is deionized water, and rinsing is carried out by flooding, dipping, or spraying, as appropriate, at a suitable temperature. Rins-

ing may be more or less aggressive, including mechanical scrubbing or by means of a high-pressure spray, or merely soaking the substrate in the rinsing medium without mechanical action.

[0065] The substrate may also be contacted with a conditioning agent, which is a substantive material, commonly a cationic material such as a polyamidoamine, a cationic polymer, a cationic surfactant, or the like. Most broadly, the conditioner is an alkaline aqueous solution or dispersion of a conditioning agent. Suitable conditioning agents include, for example, SANDOLEC CF, SANDOLEC CU, SANDOLEC CS, SANDOLEC CL, SANDOLEC CT, (Novartis, Basel, Switzerland, formerly Sandoz Chemical Company) CALL-AWAY 6818 (ExxonMobil, Irving Texas), CYASTAT SP, CYASTAT LS, CYASTAT SN, CYANAMER A-370 (BASF, Mount Olive, New Jersey), and combinations thereof comprising at least one of the foregoing agents. The conditioning agent is applied as an adhesion promoter so the substrate will be attractive to the anionic particles of carbon, which are later applied by contacting the substrate with the carbon dispersion.

[0066] A substrate may be dip-processed in the conditioning solution, or conditioned in a conveyORIZED process by flood-

ing, also, cleaning and conditioning can be combined into a single operation prior to the application of the carbon dispersion. Thus, the substrate is cleaned and conditioned by contacting it with an alkaline aqueous solution or dispersion of a surfactant and a conditioning agent.

[0067] After the substrate is cleaned and conditioned, and (optionally) before or after adhesion to the substrate is promoted, the surface is contacted with a liquid carbon dispersion as previously described. The carbon dispersion is applied from a bath or by flooding in most instances. Preferably, after contacting the substrate with the carbon dispersion and before drying it, the dispersion may be fixed, for example, by chemical fixing or physical fixing.

[0068] Chemical fixing includes applying a fixing solution to the surfaces that have been wetted by the carbon dispersion. The fixing solution removes excessive carbon composition deposits, crosslinks the first monolayer of carbon that is directly attached to the substrate, and thus smoothes the carbon coating on the substrate by eliminating lumps and by making the coating uniform. The fixing solution may be water, aliphatic or aromatic solvents, or a dilute aqueous acid. If water is used, the water may first be warmed to about 49°C to 60°C to effect fixing, while the dilute acid

solution is capable of fixing the bound carbon at room temperature or warmer. Fixing is typically accomplished by an exposure of the carbon coating to the fixing solution of about 30 seconds to about 60 seconds.

[0069] Typical acid fixing solutions include dilute aqueous solutions containing about 0.1 to about 5% by volume acid. Suitable acids include mineral acids, such as hydrochloric, phosphoric, nitric, or sulfuric acid. Organic carboxylic acids, such as acetic acid, citric acid, and others, may also be used. A specifically contemplated fixing solution is a dilute aqueous solution of sulfuric acid, such as an aqueous solution containing about 0.1% to about 2% sulfuric acid by volume. Acidic fixing solutions that contain less than 0.1 vol% acid may require some heat to effect fixing within the about 30 to about 60 second exposure.

[0070] An effective acid fixing bath generally contains sufficient acid to provide a pH of about 0.01 to about 7, alternatively about 0.1 to about 4, by using about 0.1 to about 0.5% by volume of concentrated sulfuric acid in deionized water. The normality of the acid may be from about 0.01N to about 10N. The bath may be used at room temperature, for example, about 20°C, or alternatively from about 35°C to about 70°C.

[0071] In physical fixing, the substrate wetted with the carbon dispersion may be subjected to a mechanical force that removes excess deposits of the carbon coating before it is dried. The mechanical force may be applied in a wide variety of ways including, for example, the action of a fluid jet contacting the surface that has been coated with the carbon dispersion. The fluid jet can be a jet of air or another gas directed at the treated substrate to blow away any excess accumulations of the carbon deposit, and particularly any occlusions of the carbon dispersion, which can produce undesirable results.

[0072] For example, an air jet can be provided in the form of an "air knife" (i.e., a curtain of moving air). The curtain is commonly stationary, and includes air or another gas traveling perpendicular to the surface of substrate, through which the substrate is passed to blow off and thus fix the carbon dispersion thereon. The air pressures contemplated for use in an air knife process are typically about 2 to about 3 N/cm² (Newtons per square centimeter), or more broadly equal to or less than about 2 N/cm² to about 20 N/cm² or more. The curtain of air may also be heated to further assisting in drying the substrate.

[0073] After the carbon dispersion is applied and optionally

fixed, the carbon-coated portion of the substrate typically is dried, thus depositing a dry carbon coating on the substrate. The substrate may be dried in an oven. Drying may be accomplished by using heated air (in the fixing step or later), by employing heat lamps or other radiant heat sources, by simple air-drying at ambient temperature, or by other drying techniques. Typical drying conditions include oven-drying for about 15 to about 18 minutes at about 60°C to about 82°C.

[0074] When the substrate is being prepared for additional processing, it is possible to remove the carbon dispersion coating and other residues from surfaces not requiring the carbon layer by any number of processes, for example microetching, in which the carbon-coated substrate is treated with an etchant to remove a slight amount of the substrate surface, without appreciably attacking the carbon coating or the non-carbon clad surfaces. The carbon coating typically is sufficiently porous to allow the underlying substrate to be attacked. When the underlying surface to which the carbon deposit adheres is microetched, the carbon deposit flakes away from the surface while remaining intact in other areas. The substrate is preferably then rinsed to remove residual flakes of carbon and to

maintain the integrity of the subsequent reagents. Microetching compositions are used in connection with carbon dispersion coating processes and include, for example, the formulation described in U.S. Patent No.

5,139,642, as well as others. Microetching compositions may be deployed by dipping the substrate in a microetch bath or by spraying the substrate with a microetch composition. The result of microetching being surfaces once covered are freed of the carbon deposit, while other areas retain the deposit and thus remain conductive and protected. The etched surfaces thus can form connections with other components.

[0075] It is also desirable to treat the surfaces of the substrates with an anti-tarnishing agent, which prevents corrosion of the surfaces. Anti-tarnishing agents and treatments include the agent described in U.S. Patent No. 5,139,642, as well as others. After the anti-tarnish step, the substrate is preferably rinsed.

[0076] After the surfaces are coated with a carbon layer, they are commonly dried prior to subsequent processing.

[0077] In some instances, it may be desirable to repeat some of the process steps previously defined. For example, the process can be carried out with the following sequence of

steps, including some repetitive steps compared to the "single-pass" process which has been described so far, such as, for example, cleaning/conditioning, rinsing, contacting with carbon dispersion, drying, cleaning/conditioning, rinsing, contacting with carbon dispersion, drying, microetching, rinsing, anti-tarnish treating, rinsing, and drying. Each step of the foregoing double-pass process can be carried out mostly or entirely like the corresponding step of a single-pass process.

[0078] In some instances, the carbon-coated surface may also be electroplated. An example of an electroplating process is disclosed in U.S. Patent No. 5,139,642.

[0079] When the carbon coating is complete, the deposited material is preferably resistant to being pulled away (which resembles a blister in the plating) and other adhesion defects, even when the most severe thermal shock tests are performed.

[0080] The coated substrate has an electrical resistivity of equal to or less than about 1000 ohm-centimeters (ohm-cm), preferably equal to or less than about 10 ohm-cm, and more preferably equal to or less than about 1 ohm-cm.

[0081] A thin, uniform coating of the carbon composition on the substrate surface aids to maintain proper sealing of the

components of the cell and adequate electrical conductivity.

[0082] Preferably the coating will be nearly as thin as the diameters of the dispersed particles of carbon, so it will form a monolayer of carbon particles. For example, a composition containing one-micrometer mean diameter particles would provide a film on the order of one micrometer thick. More particularly, the coating will be about one to about three micrometers thick. Thinner coatings are acceptable until the coating becomes so thin that complete coverage is not obtainable.

[0083] The degree of uniformity of the coating is sometimes expressed qualitatively by reporting that the coating in question exhibits, or is free of, lumpiness or localized areas having a thick coating of the carbon coating. Lumpiness (if present) typically is found at the entrance or exit of surface features on the substrate (i.e., holes, corners, studs and the like). Alternatively, the degree of uniformity of the coating may be viewed qualitatively as a coating having characteristics, as herein disclosed, that are substantially unvarying over the coated surface.

[0084] The elemental carbon coating described herein results in internal components suitable for their intended purposes.

Provided for is an improvement in coating and method of coating the internal components of an electrochemical cell, particularly regarding enhancing electrical conductivity within the electrochemical cell while providing an inert surface. Consequently, lower cost materials may be used within the cell, and other materials, which were not compatible with the current technology, may now allow a more robust cell design.

[0085] While the invention has been described with reference to an exemplary embodiment, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof.

Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

[0086] What is claimed is: